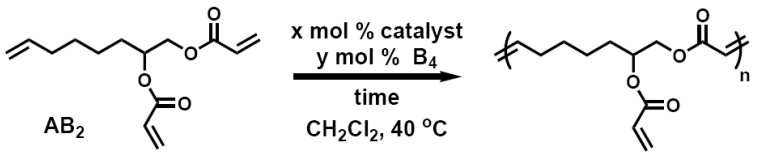
CHAPTER 4

Towards Molecular Weight Control of the Hyperbranched ADMET Polymerization

Abstract

This chapter presents an investigation of the factors thought to be capable of influencing a hyperbranched ADMET polymerization. More specifically, the catalyst loading, reaction time, and use of mono- and multi-functional additives were considered in this study. Unexpectedly, the polymerization system response to these tests strongly suggested pseudo-chain-growth, rather than clear step-growth, kinetics expected of addition polymerizations. A catalyst "branch-hopping" mechanism consistent with the observed polymerization behavior is proposed.



Introduction

Hyperbranched polymers are polydisperse, three-dimensional macromolecules with a densely functionalized semi-globular periphery.[1-6] These structures are closely related to monodisperse dendrimers and are also typically prepared from $AB_n \geq 2$ type monomers. However, unlike the latter, hyperbranched polymers are synthesized by a one-pot, poorly controlled polymerization, in which unprotected functional groups A and B react with each other but not with themselves. Although hyperbranched polymers lack the uniformity of dendrimers, they possess many of the attractive dendritic features such as good solubility, low viscosity, and multiple end groups. Consequently, the available simple synthetic routes to hyperbranched architectures make these polymers especially appealing candidates for bulk property applications, as components of blends, additives, and coatings.[1,2,7]

Regardless of the type of application, a thoroughly understanding and controlling the molecular weight and polydispersity of a polymer is essential for deriving structure–property relationships and tuning material properties.[8] Among numerous reported hyperbranched polymerization methods,[1-6] polycondensations and polyadditions of AB_n monomers are usually the simplest and the least expensive, but these step-growth processes are also the most difficult to control.[8] Nevertheless, a number of factors which improve the efficiency of these reactions (such as high temperatures,[1,7,9] extended reaction times,[1,7] and the choice of solvent)[9] have been shown to increase the size of the resulting polymers. On the other hand, the addition of end-capping reagents has been demonstrated to decrease the molecular weight of hyperbranched chains.[10] In addition, and more specific to dendritic growth control, multifunctional B_f core molecules have also been utilized, and they appear to reduce the polydispersity index (PDI) of the hyperbranched products, although at the expense of size.[11-15] However, catalyst loading as a regulatory tool for transition metal catalyzed hyperbranched polyadditions remains undeservingly overlooked.

We have recently reported a facile approach to the synthesis of hyperbranched polymers via ruthenium catalyzed acyclic diene metathesis polymerization (ADMET).[16] This transition metal catalyzed polyaddition is based on the selectivity of the imidazolinylidene catalyst **1** (Figure 4.1) in the cross metathesis of different types of

olefins. Since **1** effects a selective cross between an electron rich terminal aliphatic alkene and an electron poor acrylate, compounds such as the AB_2 monomer **2** (Scheme 4.1) form highly branched structures (**3**) in its presence.[16] The previously described reaction conditions, which employ a fixed amount of the catalyst and no additives, reliably afford the polydisperse, modestly sized polymer **3** in excellent yields. However, in an attempt to gain a better understanding of this polymerization process and, ultimately, better control it, we have investigated several potentially influential factors. Herein, we report our advances in the optimization of the hyperbranched ADMET polymerization conditions by exploring the effect that catalyst loading, reaction time, and inclusion of multifunctional core molecule (**4**) have on the molecular weight and polydispersity of **3**.

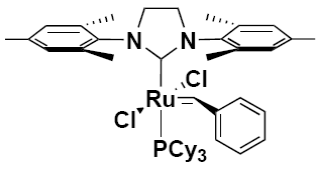


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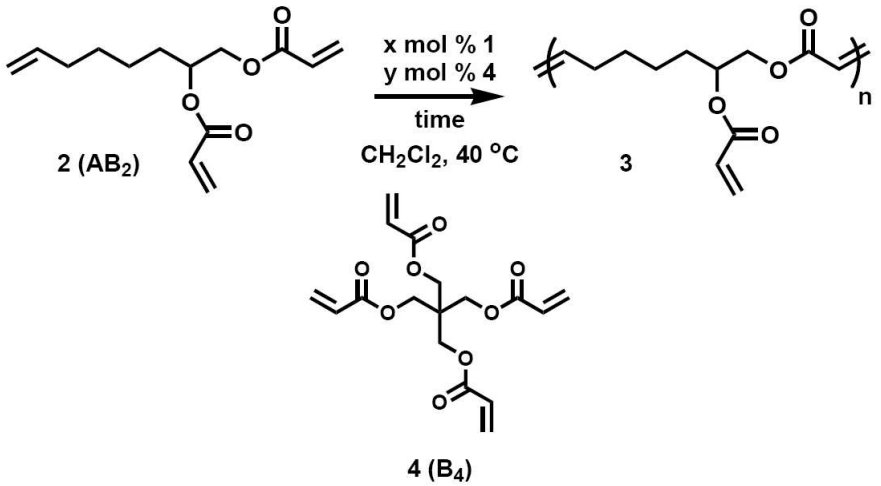
Figure 4.1. ADMET catalyst **1**.

Scheme 4.1. Hyperbranched ADMET Polymerization.



Results and Discussion

Catalyst Loading. Addition polymerizations of AB_2 monomers are traditionally thought of as step-growth processes, in which a build-up of oligomers precedes a sharp increase in molecular weight at high conversions. Consequently, the efficiency of the chosen polymerization reaction is crucial for obtaining high molecular weight polymers. Therefore, if a larger amount of the catalyst increases the effectiveness of the catalyzed reaction, it should also boost the molecular weight of the produced polymers. In fact, this trend was observed for some hyperbranched polycondensations.[1,2,7] However, contrary to any such expectations, increasing the amount of catalyst **1** from 0.5 mol % (red trace) to 1.0 mol % (blue trace) and 5.0 mol % (green trace) caused the molecular weight of **3** to diminish from 6.8 kDa to 4.1 kDa and 1.4 kDa respectively (Figure 4.2A).

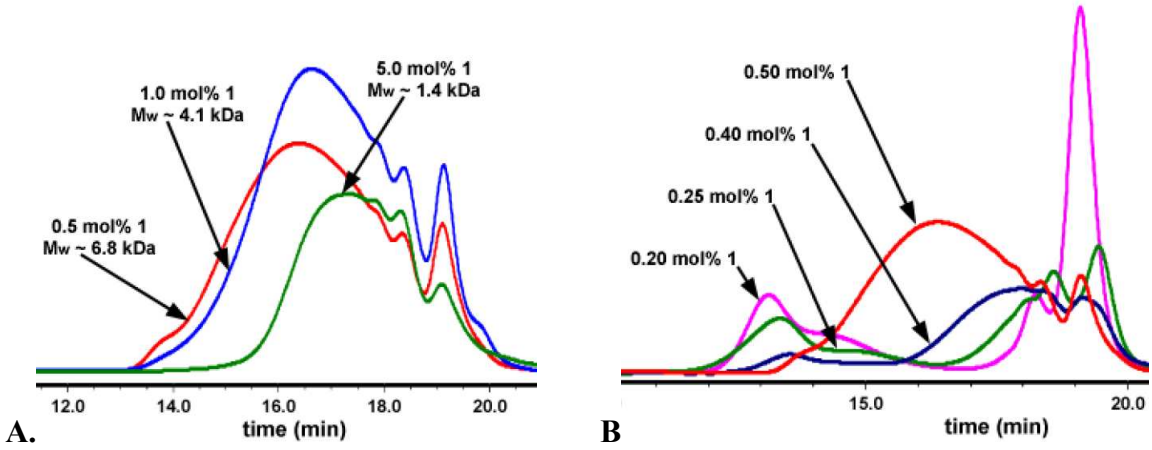


Figure 4.2. SEC (RI) traces for **3** made with different amounts of **1**.

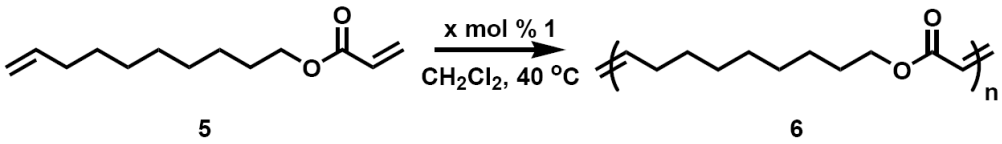
To expand upon our findings, we reduced the amount of catalyst in the polymerization of **2**. As shown in Figure 4.2B, increasing the monomer to catalyst ratio yielded materials with not only much larger chains in the reaction mixture, but also with quite different SEC profiles. The most prominent feature of these traces is their enormous polydispersity; the broad PDI is visually evident in Figure 4.2B, where the samples obtained from the polymerizations with less than 0.5 mol % of **1** appear to contain almost no intermediate sized polymers but, rather, contain only high molecular weight chains (peaks at ~ 13 min) and small oligomers (~ 19 min). By comparison, at a

0.5 mol % catalyst loading, all the peaks merge into a smoother, average trace with an improved PDI.

An important feature of catalyst **1** is benzylidene moiety. The benzylidene transfers to the growing polymer or monomer as a styrene group, potentially end-capping the growing chain after the first catalytic cycle of **1**. Consequently, some of the molecular weight behavior observed for **3** can be attributed to changes in the number of these growth terminating groups, which correlates with changes in the amount of catalyst. Therefore, a higher catalyst loading also furnishes more end-capping species during the polymerization and, thus, results in shorter polymer chains, but less catalyst has the opposite effect on the polymerization. However, it is unlikely that the catalyst and its counterparts are solely responsible for all of the observed behavior because the molecular weight fluctuations are too large.

A "linear" polymerization of an AB monomer **5** (Scheme 4.2) was investigated next in order to 1) probe the influence of the architecture of the growing chain on the polymerization kinetics and 2) separate any such effects from those associated with specifics of ADMET with **1**. Figure 4.3 presents the SEC traces for **5** produced with different amounts of **1**. As expected of an addition polymerization, more catalyst promotes more efficient cross metathesis and higher molecular weights. In particular, increasing the catalyst loading from 0.25 mol % (green trace) to 0.50 mol % (red trace) and 1.00 mol % (blue trace) resulted in the molecular weight of **5** increasing from 7.3 kDa to 8.5 kDa and 9.1 kDa, respectively. However, more than 2.5 mol % of **1** causes the molecular weight to drop dramatically, which is, most plausibly, the manifestation of end-capping by the styrene produced from catalysis with **1**.

Scheme 4.2. Linear ADMET polymerization.



5 **6**

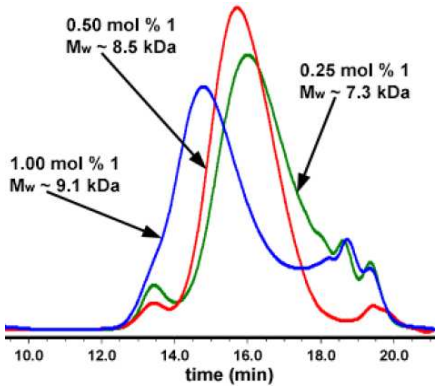


Figure 4.3. SEC (RI) traces for **5** made with different amounts of **1**.

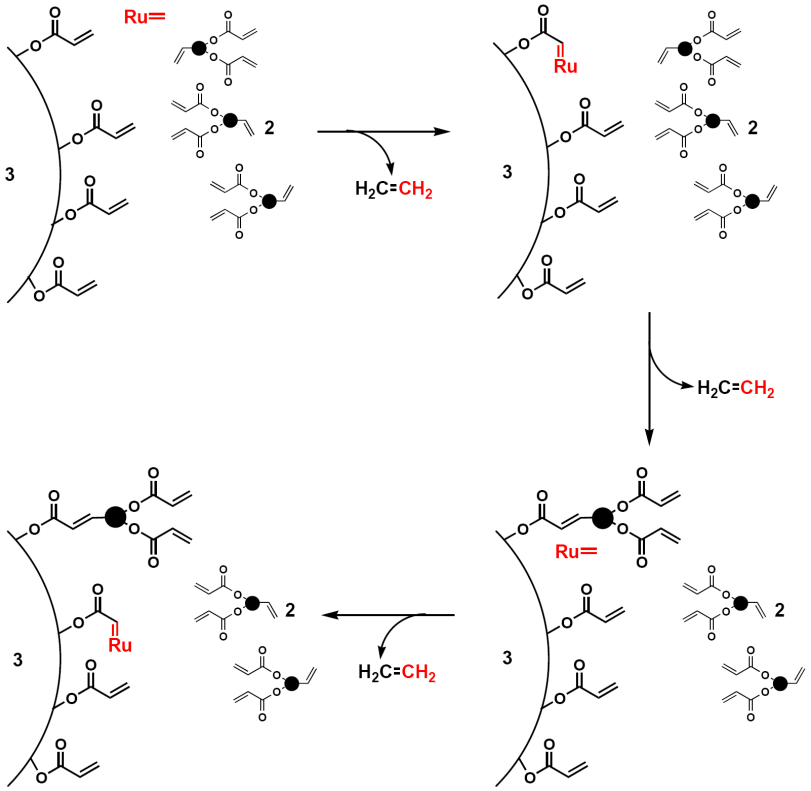
The linear ADMET polymerization of **5** clearly indicates that the unusual polymerization behavior of AB_2 monomers is due to hyperbranched architecture of the growing polymer and not catalyst **1** or the ADMET reaction itself. Furthermore, the dependence of the molecular weight on the catalyst loading demonstrated by **3** is strongly reminiscent of chain-growth kinetics—the monomers (from the small molecular weight peak) are added to the growing chain (large molecular weight peak). This differs from the step-growth kinetics expected for an addition polymerization and, indeed, observed for **5**. Moreover, less **1** seems to produce fewer but larger chains than does more catalyst, and it appears from the SEC analysis that for very low catalyst loadings, **1** decomposes before all of the monomers and smaller oligomers are consumed (Figure 4.2B).

The important difference of the hyperbranched architecture of emerging **3** is its multiple end-groups, which allow for more monomer addition opportunities, relative to the linear architecture of **6**, where only two end-groups are available for addition at any given time. Consequently, once an initial multifunctional, hyperbranched oligomer is formed, a high local concentration of acrylates is created, and the probability of a monomer adding to the growing chain is higher, than the probability of two independent monomers finding each other in solution. However, other factors must also influence the observed molecular weight–catalyst loading relationship; otherwise, more catalyst would be expected to further increase the monomer addition efficiency and produce larger, not smaller polymers.

An additional rationale may underlie the catalyst loading dependence of the hyperbranched ADMET polymerization: at low catalyst loading, the majority of the

active catalytic species in the reaction mixture are "stuck" to the densely acrylate populated periphery of the growing chain. In this case, monomer additions in the polymerization of **2** are only occurring along the polymer chain's outer sphere, as the catalyst "walks" around it—a chain-growing mechanism depicted in Scheme 4.3. According to this mechanism, as **1** initially reacts with any of the peripheral acrylates of **3**, it becomes physically attached to the growing chain. Although the metal carbene is then quickly released through addition of a monomer (**2**) to the polymer, the freed catalytic species remain surrounded by many more peripheral acrylates. Therefore, it is much more likely that the catalyst is recaptured by **3** and continues its chain-growing "walk" along the periphery, instead of completely dissociating from the polymer to connect two independent monomers in a step-growth fashion. On the other hand, the larger amount of **1** in the reaction mixture increases the probability of unbound catalytic species in the polymerization solution, which, in turn, ensues competitive step-grows.

Scheme 4.3. The "chain-walking" mechanism for hyperbranched ADMET polymerization at low loading of **1**.



Reaction Time. Another important factor in the molecular weight control of a hyperbranched polymerization is reaction time. The duration of the polymerization reaction is particularly important in the case of step-growth, since high monomer conversion is crucial for progressing the polymerization beyond oligomers. Indeed, the molecular weight of **3** does seem to increase with prolonged reaction times, and the PDI is also improved (Figure 4.4); but these changes are modest. Furthermore, the uncertainty of the SEC measurements might be partially responsible for the apparent "jagged" shape of the traces in Figure 4.4A. On the other hand, the molecular weight dips in the time plot (which are especially pronounced for the higher molecular weight polymers obtained at lower catalyst loadings in Figure 4.5A) could also be caused by polymerization "errors"—internal aliphatic alkenes (A-A links). As these undesirable backbone connections are cleaved by the "correct" A to B monomer additions, more thermodynamically stable and olefin cross metathesis resistant A-B links are formed (Figure 4.5B). If the "error correction" assumption is true, it further substantiates the catalyst "branch-hopping" hypothesis. Any A-A defect would quickly become buried in the polymer backbone during the polymerization and would be hard to reach for the cross metathesis catalyst, unless the catalyst directly stumbles onto such a "weak" link during the periphery walk.

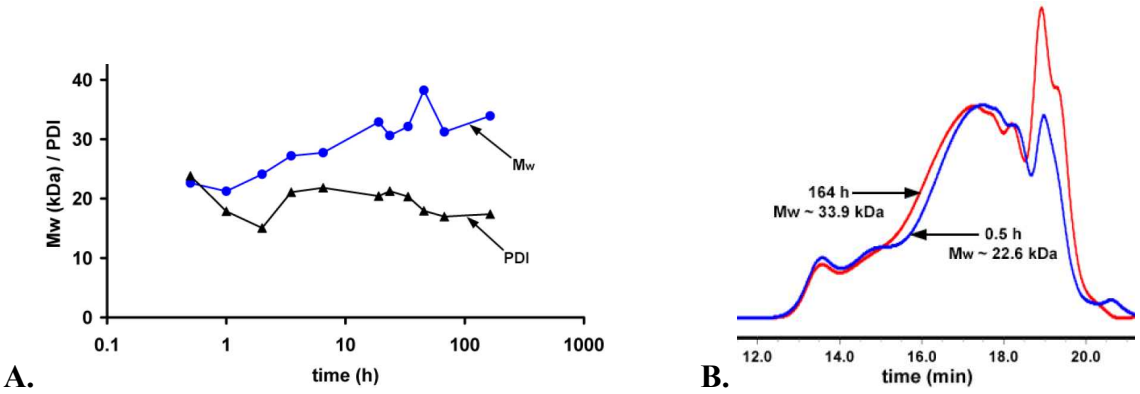


Figure 4.4. Molecular weight and PDI timeline of **3** at 0.5 mol % of **1**.

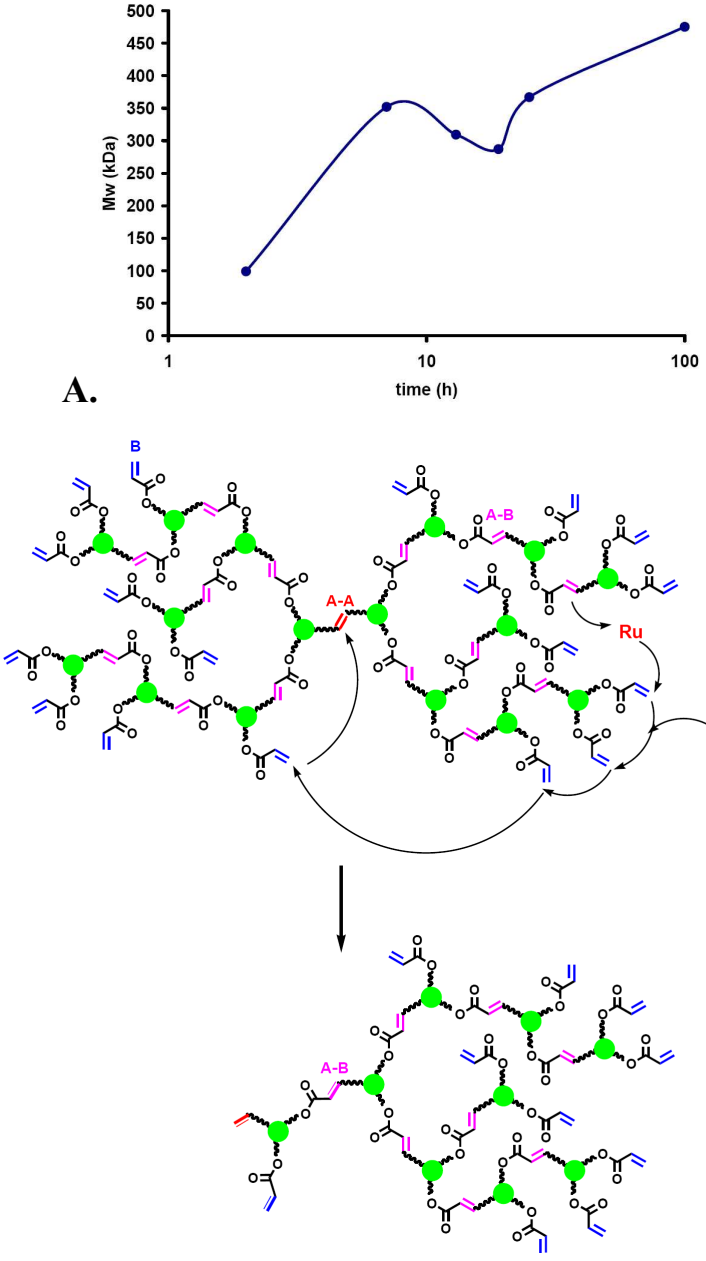


Figure 4.5. Proposed polymerization "error" correction mechanism.

Figure 4.6 illustrates additional experiments, which relate molecular weight to both reaction time and end-capping; here, a polymerization is quenched at different times by addition of 8-bromo-1-octene. As evident from the presented SEC traces, the addition of 1 equivalent of bromooctene (relative to the monomer) efficiently stops the molecular weight build-up. Specifically, when the polymerization of **2** with 0.5 mol % of **1** was allowed to proceed for 72 hours without the addition of bromooctene, the molecular

weight of **3** reached 7.1 kDa (red trace). However, addition of end-caps at 12 hours (green trace) or 24 hours (blue trace) reduced this value (still measured at 72h) to only 3.3 kDa and 4.2 kDa, respectively. One of the important implications of these quenching experiments is that the one-pot synthesis and functionalization of **3** might be possible, if the end-capping reagent also carries an analyte.

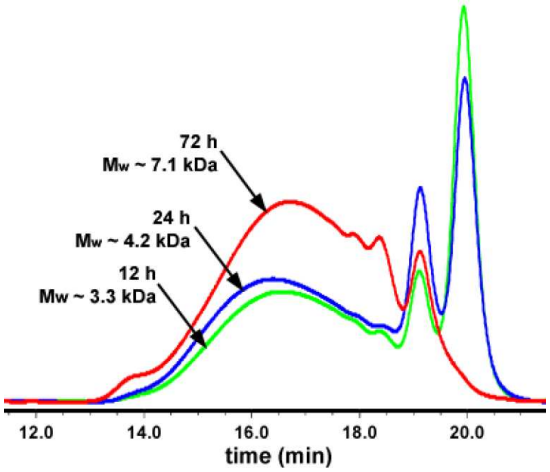


Figure 4.6. The dependence of the observed M_w at 0.5 mol % of **1** on the addition time of 8-bromo-1-octene.

Addition of a Multifunctional Core. Finally, the effect of a B_4 core (**4**) on the molecular weight and PDI of **3** was investigated. Figure 4.7 illustrates the outcome of the introduction of different amounts of **4** to the polymerization of **2** with 0.5 mol % (Figure A) and 0.2 mol % (Figure B) of **1**. According to Figure 4.6A, polymerization with a larger amount of catalyst appears to be influenced by the core molecules as expected, and increasing the amount of **4** lowers the molecular weight of **3**, while slightly improving its PDI.[11-15] In essence, **4** acts as a multifunctional growth terminator unit, which quenches the polymerization when present at high concentrations (low monomer to core ratio).[15]

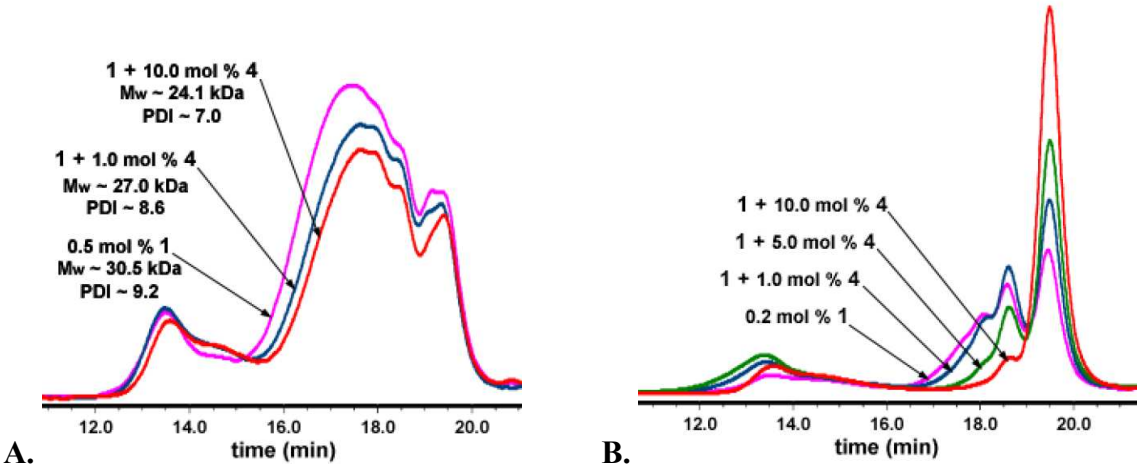


Figure 4.7. SEC (RI) traces for **3** made with a fixed amount of **1** (0.5 mol % in Figure A and 0.2 mol % in Figure B) but different amounts of **4**: none (pink), 1.0 mol % (blue), 5.0 mol % (green), and 10.0 mol % (red).

The situation is quite different for polymerization with smaller amounts of **1** (Figure 4.7B); the SEC traces for these samples have a bi-modal distribution of molecular weights. The addition of increasing amounts of **4** (pink to blue to green traces) results in 1) an increased molecular weight for the left-hand, already high molecular weight peaks (they shift further to the left), and 2) the simultaneous narrowing of the right-hand, oligomeric peak. At very high concentration of **4** (10 mol %, red trace) this relationship breaks down (left side of the trace), with smaller polymers produced in the polymerization.

We believe that the observed effect of the B_4 core on the ADMET polymerization of AB_2 **2** further confirms the catalyst "branch-hopping" hypothesis, especially at low catalyst concentrations. In line with this hypothesis, it appears that the multifunctional core molecules serve as catalyst sponges, and, consequently, chain-growth initiators (Scheme 4.3). At low concentrations of **1**, and at concurrent high concentrations of **4** in the polymerization solution, the catalyst capture is very efficient, and the oligomer build-up is restricted. Fewer oligomers results in a larger pool of monomers for chain growth addition to the periphery of the hyperbranched macromolecule and larger polymers are produced. An excess of B_4 quenches the polymerization entirely and produces much smaller chains, but, still, almost no oligomers (red trace in Figure 4.6B). However, at

higher catalyst loadings, some catalyst can escape trapping and promote the competing step-processes of oligomer formation.

Conclusion

The utility of hyperbranched polymers can be greatly expanded by controlling molecular weight and polydispersity during their production. To accomplish this goal, the factors implicated in influencing the molecular weight and PDI of the ruthenium catalyzed hyperbranched ADMET polymerization were investigated. It appears that at low catalyst loading the polymerization follows pseudo-chain-growth kinetics, rather than the step-growth kinetics expected for polyadditions of AB_n monomers. Moreover, the synthesis of these polymers can be controlled by the catalyst loading, the use of multifunctional cores, and, to some extent, the reaction time. This polymerization behavior seems to stem from the hyperbranched architecture of the growing chains, and a mechanism, which relies on high local concentration of the multiple end groups associated with such an architecture, is proposed. An important implication of the purported mechanism is that the chains obtained from lower catalyst loadings might be more uniform and dendrimer-like. Although the studies described in this report were conducted specifically for ADMET, the findings may prove general to transition metal catalyzed hyperbranched polymerization methods.

Experimental Procedures

Materials. All reagents, except for catalyst 1, were purchased from Aldrich at the highest available purity and used without further purification. Catalyst **1** was obtained from Materia, Inc. The synthetic procedures with full characterization for **2** and **5**, along with the procedures for their polymerization with **1** (to **3** and **6** respectively), have all been previously reported.[16] When working with hyperbranched polymers of higher molecular weight, it is highly advisable to use the properly silylated glass or plastic tare, to prevented any acid-catalyzed crosslinking of the multiple acrylate groups present on the periphery of the chains.

Instrumentation. NMR spectra were obtained using a Varian Mercury-300 spectrometer; samples were dissolved in CD_2Cl_2.

Size exclusion chromatography (SEC) analysis was performed using a Wyatt triple detector system equipped with a triple angle light scattering (miniDAWN TREOS, with a laser wavelength of 658 nm) detector, a viscometer (ViscoStar) detector, and a refractive index (Optilab rEX) detector—all operating at 25 ^{o}C. Viscotek ViscoGEL I-Series (one mixed bed medium MW and one mixed bed high MW) columns were used for SEC with THF as the eluent and a Shimadzu LC-10AD pump operating at 1.0 mL/minute.

Synthesis of B4 core (4). Clear, yellowish oil **4** was made from a well-dried pentaerythritol according to the general procedure previously outlined for **2**.[16] ^{1}H NMR (300MHz, CD_2Cl_2, ppm): δ 6.38 (dd, J = 17.1 Hz, J = 1.5 Hz, 4H), 6.12 (dd, J = 17.4 Hz, J = 10.5 Hz, 4H), 5.86 (dd, J = 10.2 Hz, J = 1.2 Hz, 4H), 4.28 (s, 8H). ^{13}C NMR (300MHz, CD_2Cl_2, ppm): δ 165.97, 131.83, 128.31, 63.18, 42.73. HRMS(FAB+) m/z: 353.1247 [M+H].

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